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Novel donor–acceptor triple mesogens incorporating disc-like and rod-like molecular sub-units

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Novel non-symmetric charge-transfer trimers are presented which consist of an electron-rich penta-alkynylbenzene group with different peripheral substituents and a flat nitrofluorenone acceptor moiety both of which are chemically linked to the terminal positions of a rod-like azobenzene unit. The laterally unsubstituted member of the pentayne based CT-triple compounds and the five-fold methyl modified homologue exhibit an enantiotropic mesophase which can be obtained as a frozen-in glassy state at room temperature. The X-ray investigations reveal a nematic columnar ($N_{C_{01}}$) like molecular arrangement for the mesophases of both compounds. The columns are formed through an intercalated stacking of the flat donor and acceptor sub-units of different molecules. The rigid rod-shaped moieties are aligned with their long axes orthogonal rather than parallel relative to the columns axis. A further elongation of the five lateral alkyl substituents of the donor group enhances the steric frustration between the disc-like and the rod-like molecular groups and the five-fold pentyl substituted pentayne donor–acceptor trimer no longer exhibits mesomorphic properties. Dielectric investigations confirm the occurrence of a glass transition well below the clearing temperature and reveal the presence of thermally activated secondary relaxation processes in the low temperature range. For these trimers containing an azo group, an additional secondary relaxation (β_2 -process) is observed, which is probably caused by a local motion of the azo group within the spacer segment.

1. Introduction

The character of thermotropic liquid crystalline phases is predominantly determined by the anisometric geometry of the constituent molecules. A rod-like molecular shape usually causes the formation of nematic and/or smectic mesomorphic structures, whereas molecules possessing a flat or nearly flat rigid core surrounded by a certain number of peripheral long chain alkyl substituents are known to exhibit nematic discotic and/or columnar mesophases.

Intermediates between classical rod-like and disc-like mesogens were initially realized with catenated compounds characterized by a long rod-like rigid core ending in two half-disc moieties [1]. These hybrid molecules can exhibit nematic, smectic and columnar phases.

A further approach towards molecules bridging the gap between calamitic and disc-shaped mesogens con-

sists in the covalent linkage of molecular sub-units with different anisometric shapes via flexible alkyl spacers. Examples are non-symmetric dimers composed of flat penta-alkynylbenzene moieties linked chemically with rod-shaped cyanobiphenyl units [2] and trimers consisting of two disc-shaped triphenylene cores which are connected via a rod-like rigid group [3].

In addition to the design of new molecular architectures by combining disc-like and rod-like mesogenic groups in a defined manner within one molecule, the combination of an anisometric sub-unit with an additional intramolecular functionality offers a powerful tool to create novel supramolecular structures [4]. This approach involves for example the chemical linkage of a flat anisometric donor moiety with a molecular sub-unit acting as an electron acceptor via a flexible spacer. Thus, non-symmetric charge-transfer (CT) twin molecules based on flat electron-rich triphenylene groups decoupled from an intramolecular acceptor function

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by spacers of different lengths were reported to form columnar mesophases with either an orthorhombic or a hexagonal two-dimensional lattice [5].

More recently, we presented donor–acceptor twin mesogens which consist of pentayne donor moieties with different peripheral substituents chemically linked with nitro-substituted fluorenone sub-units via flexible alkyl spacers [6]. The mesophase structure of these dimers is characterized by a columnar arrangement on a two-dimensional rectangular array with a regular periodic intracolumnar ordering. The donor and acceptor moieties of the molecules are placed in an alternating manner within neighbouring columns. In at least one case, these special features gave rise to a novel rectangular columnar plastic (Col_{rp}) phase with a three-dimensional crystal-like correlation of ordered columns [7]. The additional incorporation of an asymmetric carbon into the spacer sequence resulted in pentayne based CT-twin mesogens displaying a nematic columnar mesophase with a helical twisting of the columns ($\text{N}_{\text{coi}}^{\text{c}}$) [7].

It is well known that charge-transfer interactions between flat aromatic electron donors such as triphenylene ethers or multialkynylbenzene derivatives with acceptor molecules may cause the stabilization as well as the induction of columnar mesophases [8–10]. Yet the chemical linkage of the donor with an acceptor molecular sub-unit gives rise to liquid crystalline structures that cannot be achieved by simply mixing the two components.

Consequently, the general question arises whether further control of mesomorphic structure formation might be possible by the covalent linkage of three different structural elements within one molecule, in particular, by combining a disc-like electron donor moiety, a rod-like molecular sub-unit and an intramolecular acceptor function (figure 1).

This concept has been realized with the non-symmetric trimers **4** (figure 2). These consist of a sheet-like electron-rich penta-alkynylbenzene group and a flat nitrofluorenone

based acceptor group which are chemically linked via a rigid rod-like sub-unit incorporating an azobenzene moiety. We will focus here, in particular, on the synthesis, the thermal properties and the dynamic behaviour of the novel CT-triple compounds **4a–c**.

2. Results and discussion

2.1. Synthesis

The synthesis of the donor–acceptor molecules **4** carrying an azobenzene unit within the spacer sequence was performed starting from the radial pentakis-(arylethynyl)benzene derivatives **1** [6, 11, 12] carrying a terminal hydroxy group. The pentaynes **1** were converted into the appropriate benzenesulphonates **2** by reaction with benzenesulphonyl chloride under basic conditions using pyridine. Reaction of the derivatives **2** with 4-(4-hydroxyphenylazo)benzoic acid yielded the non-symmetric dimers **3** with a flat penta-alkyne sub-unit and a rod-like azobenzene moiety linked via a flexible alkyl spacer. Subsequent esterification of the remaining phenolic hydroxy group of compounds **3** with 3-(2,4,7-trinitro-9-fluorenylideneaminoxy)propionic acid [5] in the presence of *N,N'*-dicyclohexylcarbodiimide and catalytic amounts of 4-dimethylaminopyridine resulted in the trimers **4** with three different rigid molecular parts separated from each other by flexible spacer segments. The reaction sequence is presented in figure 2.

The TNF-based acceptor, the calamitic azobenzene group and also the spacer lengths were kept constant for all compounds **4**, while different peripheral substituents were attached to the pentayne units in order to influence the dimensions of the donor molecular part.

Spectroscopic data confirmed the structure of the triple molecules **4**. Full details are given in §4.

2.2. Thermal properties of the donor–acceptor triple molecules **4**

It was apparent from differential scanning calorimetry (DSC) that the laterally unsubstituted pentayne trimer **4a** and also compound **4b** with five methyl substituents exhibit a glass transition well above room temperature, followed by a second transition at more elevated temperatures which corresponds to the transition to the isotropic melt as observed by polarizing microscopy. Both donor–acceptor molecules **4a** and **4b** show either marbled or schlieren textures on cooling from the isotropic melt; these are typical for a nematic phase. The incorporation of the five methyl groups gives rise to an increase of the glass transition and of the isotropization temperature for the CT-trimer **4b** as well as to a broadening of the mesophase range. The transition temperatures as determined by DSC are given in table 1.

On the contrary, there is no indication of mesomorphic properties in the case of the five-fold pentyl

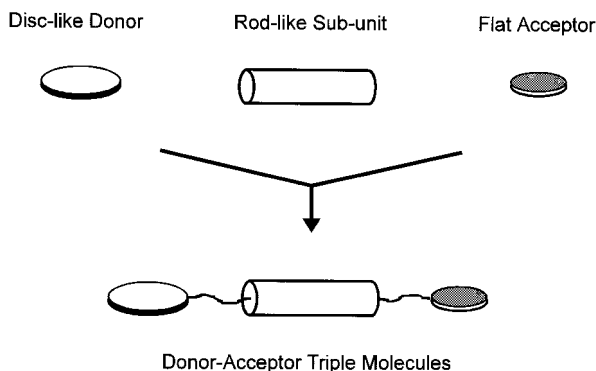


Figure 1. Charge-transfer triple molecules formed through covalent linkage of disc-like donor and acceptor moieties via a rigid rod-like molecular sub-unit.

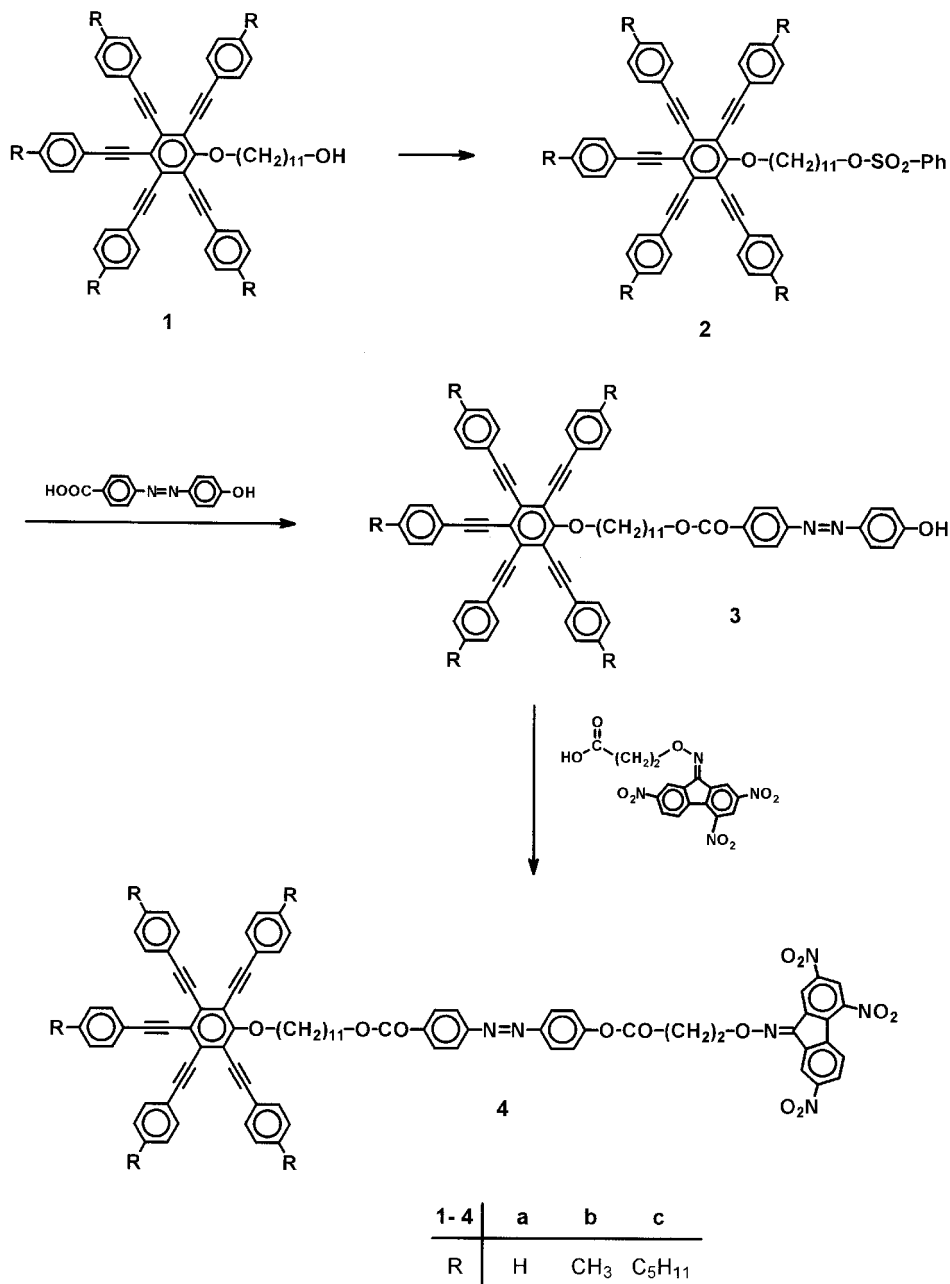


Figure 2. Synthesis of the non-symmetric trimers **4** combining a radial penta-alkyne based donor, a rod-like azobenzene group and a nitrofluorenone acceptor within one molecule.

Table 1. Phase transition temperatures (°C) for the pentayne based donor–acceptor triple compounds **4** as determined by DSC on the second heating run at 10 K min⁻¹; transition enthalpies (kJ mol⁻¹) are given in brackets. Cr = crystal; T_g = glass temperature; N_{CoI} = nematic columnar; I = isotropic.

Compound	Cr	T _g	N _{CoI}	I
4a	—	•	•	•
4b	—	•	•	•
4c	•	56.4 (49.9) ^a	—	•
	—	•	—	•

^a Observed on first heating only.

modified triple molecule **4c**. The compound melts directly to the isotropic state on first heating. Further cooling and heating cycles give evidence of a strong tendency for undercooling and only a glass transition is observed by DSC below room temperature (table 1). This result seems rather surprising since the corresponding CT-twin mesogen consisting of a pentyl-substituted pentayne donor and a TNF-based acceptor, but without an azobenzene group, has been reported as forming a rectangular columnar (Col_r) phase [7]. In addition we know that the nematic discotic (N_d) penta-alkynyl alcohol **1c** used as the starting material for the preparation of compound **4c** exhibits a CT-induced hexagonal-columnar ordered (Col_{ho}) phase in binary mixtures with 2,4,7-trinitro-9-fluorenone (TNF) [11].

On the other hand, neither the sulphonated intermediates **2** nor the non-symmetric dimers **3**, possessing both rod-like and disc-like characteristics, exhibit liquid crystalline behaviour. It follows that the enantiotropic mesophases observed for the trimers **4a,b** originate predominantly from the additional chemical fixation of the acceptor sub-unit and, hence from the charge-transfer interactions introduced thereby.

CT complex formation is confirmed by absorption spectroscopy. For example, besides a very strong absorption band in the wavelength range 300–400 nm and a shoulder at 420 nm, the UV-vis-spectrum of compound **4a** shows a weak and broad absorption band in the region 550–700 nm which peaks at 627 nm. This absorption above 550 nm can be attributed to charge-transfer interactions between the electron-rich penta-alkyne group and the strong TNF-based electron acceptor molecular part [13]. Note, that there is no hint of CT interactions between the azobenzene unit and the acceptor group since no charge-transfer bands could be detected for mixtures of TNF and azobenzene derivatives with a similar substitution pattern to that of the azo group of the compounds **4**, but without a pentayne sub-unit. Further details regarding optical properties of the CT-trimers **4** will be presented in a separate paper [13].

The X-ray diffractograms of the CT-triple mesogens **4a,b** (figure 3) display one distinct but relatively broad reflection in the small angle region corresponding to distances of 1.31 nm in the case of compound **4a** and 1.48 nm for the pentayne **4b**. The amorphous halo that appears at larger scattering angles is superimposed by a broad reflection which is indicative of a close face-to-face packing of flat aromatic cores in a column. The halo originates from a liquid-like ordering of the flexible methylene spacers.

These diffraction patterns give evidence of a columnar arrangement with only short range positional order of the columns [9, 14–16]. Consequently, it seems most reasonable to suggest that the liquid crystalline structure

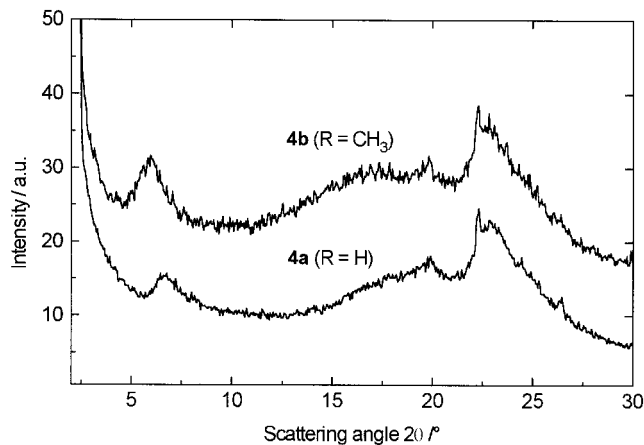


Figure 3. Wide angle X-ray diffractograms of the pentayne based donor-acceptor triple mesogen **4a** and **4b**.

displayed by the donor-acceptor molecules **4a,b** corresponds to a nematic columnar-like arrangement. This conclusion is further supported by the fact that the enthalpy observed for the transition of the CT-triple compounds **4a,b** from their mesophases to the isotropic liquid are of the same order of magnitude as those found for the clearing transitional enthalpies of charge-transfer induced nematic columnar (N_{co1}) phases formed from binary mixtures of multiethynylbenzene compounds with TNF [11, 15].

A detailed structural model cannot be derived from the X-ray pattern, and we have to speculate. Certainly, the individual columns are formed through an intercalated stacking of the flat donor and acceptor sub-units of different molecules of the CT-trimers **4**. Then one can imagine an alignment of the rod-like moieties with their long axes parallel to the column axis (figure 4(a); in this respect see also [2]). However, keeping in mind that the spacer between the calamitic azobenzene and the electron-poor nitrofluorenone moieties contains only two methylene groups and considering the large diameter of the pentayne donor units it does not seem possible to achieve such an arrangement without steric frustrations.

Alternatively, it seems more likely that the flexible spacer segments separating the flat donor and acceptor units from the rod-like molecular fragment adopt more or less stretched conformations, giving rise to an arrangement with the calamitic azobenzene units predominantly oriented perpendicular relative to the mixed columnar donor-acceptor stacks, figures 4(b) and 4(c).

A non-alternating, uniform, orientation of the CT-trimers **4** would lead to the situation that the columns are connected via quasi-chains along one direction [5] arising from the chemical linkage of the donor and acceptor sub-units of the molecules, figure 4(b). This should result in long range correlations which, however,

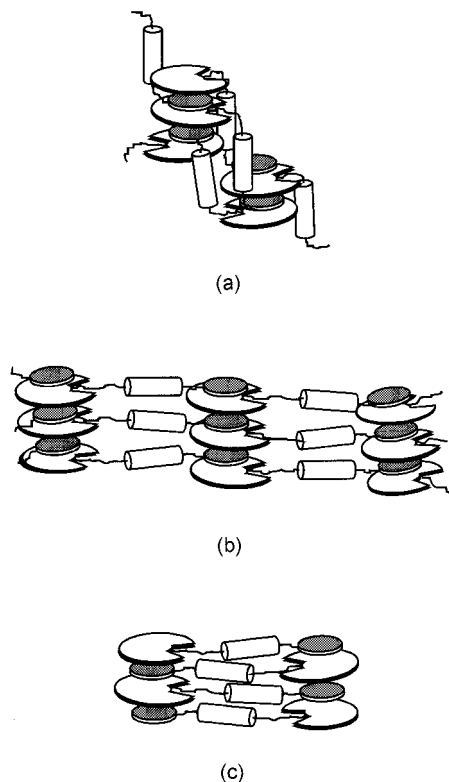


Figure 4. Two-dimensional structural models for the nematic columnar (N_{col}) mesophase of the donor–acceptor triple molecules **4a,b**. (a) Alignment of the rod-like azobenzene moieties with their long axes parallel to the mixed columnar donor–acceptor stacks; (b) rod-like molecular fragments arranged perpendicular to the columns axis with non-alternating orientation of the CT-trimers; (c) alternating arrangement of the donor and acceptor groups of the molecules in neighbouring columns separated by the calamitic sub-units. We consider here that the flat pentakis-(phenylethynyl)benzene donor molecular parts are not full discs but that the alkyl spacer is coupled to the inner phenyl ring by an ether linkage.

are not observed. A structure according to figure 4(b) would also fail to explain, for example, the low viscosity observed for the mesophases of compounds **4a,b** by polarizing microscopy.

Following these considerations, we are forced to the conclusion that an arrangement of the donor and acceptor moieties of the molecules **4** in an alternating manner in neighbouring columns, separated by the rod-like units, is most likely for the nematic columnar mesophases of the CT-trimers **4a,b**, figure 4(c).

One problem with respect to this structural model is that we cannot correlate the dimensions corresponding to the small angle reflections directly with the molecular dimensions of compounds **4a,b** along the main molecular axis which, in the case of stretched conformations of the spacers amount to approximately 5 nm (Cerius 2;

force field Dreiding 2). However, the experimental values roughly match with the diameters of the pentayne donor groups and may therefore be attributed to the mean intercolumnar distance of next neighbouring columns perpendicular to the longitudinal axis of the molecules.

Another verification for the suggested model is based on estimating the molecular density, using the dimensions which are obtained from X-ray diffraction (for **4a** $d_{intercol} = 1.31$ nm, $d_{intraol} = 0.39$ nm) and assuming a stretched conformation with $l = 5.00$ nm. A cell with these dimensions with a volume of 2.55 nm³ and containing 1 molecule on average, leads to a density of 0.9 g cm⁻³, which seems to be a good approximation for the not ideally ordered mesophase structure.

Considering the structure sketched in figure 4(c), it follows that the degree to which the relatively small acceptor groups can be inserted between the large disc-like pentayne donor molecular parts, and thus the efficiency of charge-transfer interactions perpendicular to the planes of the donor and acceptor, are limited by the spacer length between the TNF sub-unit and the calamitic moiety. Complete insertion is possible for the laterally unsubstituted penta-alkyne trimer **4a** and for the five-fold methyl modified homologue **4b**. The resulting alternate stacking of donor and acceptor groups gives rise to the enantiotropic mesophases observed here.

However, in the case of compound **4c**, the five peripheral pentyl substituents are as long as the spacer connecting the acceptor group with the rigid rod-shaped azobenzene moiety. The steric repulsion between the pentyl chains and the rod-like azobenzene group and also the short TNF spacer, prevent efficient core–core interactions in CT-complex formation and no mesomorphic properties appear.

One might expect that the nematic columnar phases of the donor–acceptor triple compounds **4a,b** displayed in figure 4(c) would exhibit biaxial properties [17]. However, preliminary conoscopic investigations† performed with **4b** did not give satisfactory results in this respect. NMR investigations on deuteriated samples would be necessary to clarify this point in more detail. Moreover, it is noteworthy that the concept of combining a disc-like donor, a rod-shaped sub-unit and flat acceptor moiety within one molecule by linking the three different structural elements chemically via flexible spacers provides a novel and powerful tool to prevent macroscopic phase separation that usually occurs in mixtures consisting of rod-like and disc-like liquid crystals [18–20].

†The authors are very grateful to D. Blunk and K. Praefcke, Technische Universität Berlin, for their assistance with respect to the conoscopic investigations and for helpful discussions regarding biaxial nematics.

The ability of the rod-like azobenzene group, placed between the donor and the acceptor moieties, to be switched by light and also the possibility of freezing the anisotropic order in a glassy state at room temperature make the CT-triple mesogens **4** promising materials for optical data storage, as is in fact evident from optical grating experiments. The results will be reported in a separate paper [13].

2.3. Dynamics of the donor–acceptor trimers **4**

Dielectric relaxation spectroscopy was used to study the freezing-in process of the discotic materials and to investigate the mobility of the various dipolar molecular units within the liquid crystalline phases. Dielectric measurements were performed in a temperature range from -160 to 200°C and a frequency range of 100 Hz to 1 MHz .

Generally, the investigated trimers showed two kinds of relaxation processes. For all compounds, a thermally activated relaxation process at low temperatures ($< 0^\circ\text{C}$) was observed, which can be described by an Arrhenius law (β -relaxation, figure 5). Furthermore, a second relaxation process was found for all compounds, this taking place at temperatures above the static glass transition. This process does not show a linear dependence in the Arrhenius plot, but it can be related to the glass transition. For the β -relaxation of **4a**, **4b** and **4c**, activation energies in the range 30 to 40 kJ mol^{-1} were found (table 2). This is in good agreement with the E_a values we reported recently for the β -relaxation of the analogous twin materials without an azo-group [7].

We suppose that this secondary relaxation process is caused by a local rotational or flipping motion of the ester group within the spacer unit [7, 21, 22]. According to the local character of this relaxation process, no significant influence of the peripheral pentayne sub-

Table 2. Activation energies for the β_1 -relaxation of the CT-trimers.

Compound	$E_a/\text{kJ mol}^{-1}$
4a	37.0 ± 0.4
4b	30.8 ± 0.4
4c	29.1 ± 0.4

stituents on the activation barriers should be expected. Nevertheless, we found a slight dependence of the activation energies of the β -relaxation: the activation energy decreases with increasing length of the alkyl group. This may be caused by small differences in the rigidity of the molecular environment dependent on the different alkyl substituents.

Comparing the relaxation curves of the CT-trimers **4a** and **4b** (H-substituted and CH_3 -substituted, respectively) to those of the corresponding dimeric twin compounds without azo groups [7], the occurrence of an additional secondary relaxation process in the case of the azo compounds is obvious (figure 6).

Compounds **4a** and **4b** show an additional shoulder at about 40 K above the main maximum (for the relaxation curve at 1250 Hz). A separation of both relaxation processes by a Lorentz fit was possible, but the error for the peak position of the weaker maximum is too big to obtain reliable information about the temperature dependence of the peak shift. Nevertheless, we were able to follow the shift of the relaxation frequency with increasing temperature from the analysis of the position of the shoulder for several relaxation curves below 5000 Hz . We found that this additional relaxation process (β_2) also follows an Arrhenius law (figure 7) with activation energies in the range 50 to 60 kJ mol^{-1} (table 3).

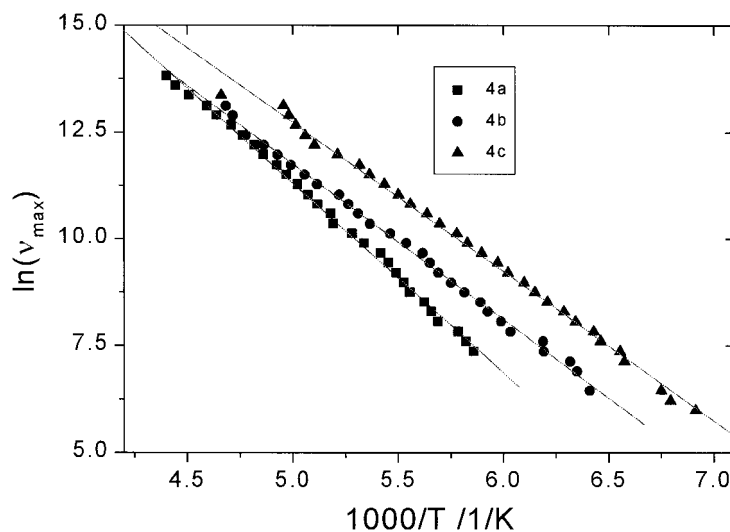


Figure 5. Arrhenius diagram for the secondary relaxation (β_1 -process) of the compounds **4a-c**.

Figure 6. Comparison of the secondary relaxation at 1250 Hz for the Me-substituted CT-trimer **4b** (with azo group) and the analogous Me-CT-twin compound [7] without an azo group.

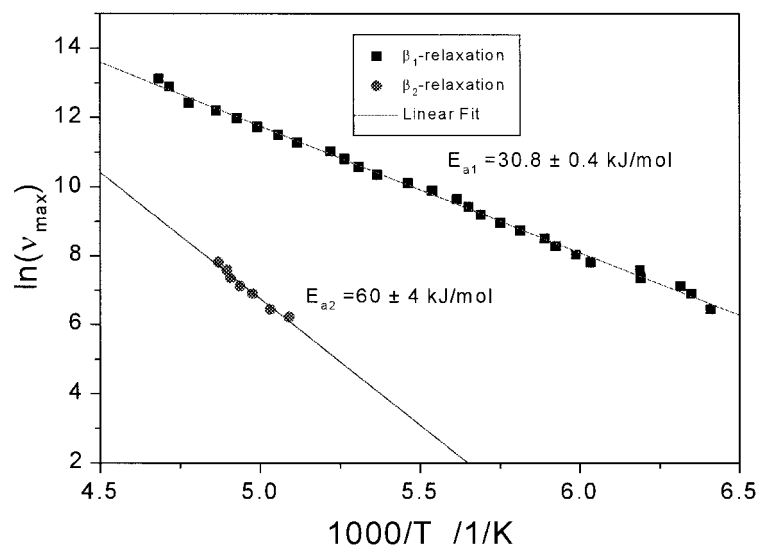
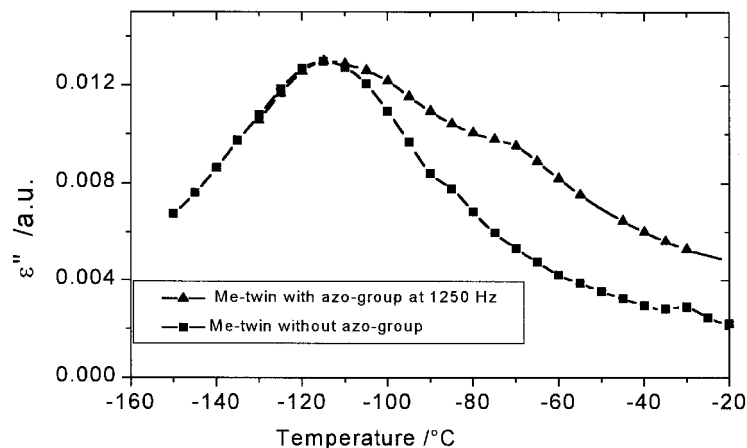


Figure 7. Arrhenius diagram of the β_1 - and β_2 -processes of the Me-substituted compound **4b**.

Table 3. Activation energies for the β_2 -relaxation of compounds **4a** and **4b**.

Compound	$\beta_2 E_a / \text{kJ mol}^{-1}$
4a	54 ± 6
4b	60 ± 4

For the pentyl-substituted trimer **4c**, the detection of an additional shoulder in the region of the β -relaxation was not possible, because in this case the glass relaxation process, shifted to a lower temperature, has already a strong influence on the curve characteristics of the β -relaxation. We suppose that the β_2 -process is caused by a local motion of the azo group within the spacer. This result is important for the understanding of photo-addressing mechanisms in these materials and indicates that the azo group of the trimer material has enough free volume to allow a slight change of orientation without appreciable steric influences on the molecular environment.

The relaxation process above the static T_g shows a relaxation strength that is about one order of magnitude larger than that of the low temperature relaxation (figure 8). In the temperature range below the clearing temperature, this relaxation is related to the glass transition (α -process) and its temperature dependence can be described by the Williams–Landel–Ferry (WLF) equation [23] (figure 9, table 4).

$$\log \left(\frac{v_T}{v_{T_g}} \right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}. \quad (1)$$

When a first-heating measurement was performed we observed a strong decrease of the relaxation strength above T_i (figure 8) and the temperature dependence strongly deviates from the WLF behaviour near T_i (figure 9).

Although the α -relaxation is still present above the clearing temperature, the decrease in the relaxation strength indicates that the correlation length of the interacting dipolar molecular units is reduced when the

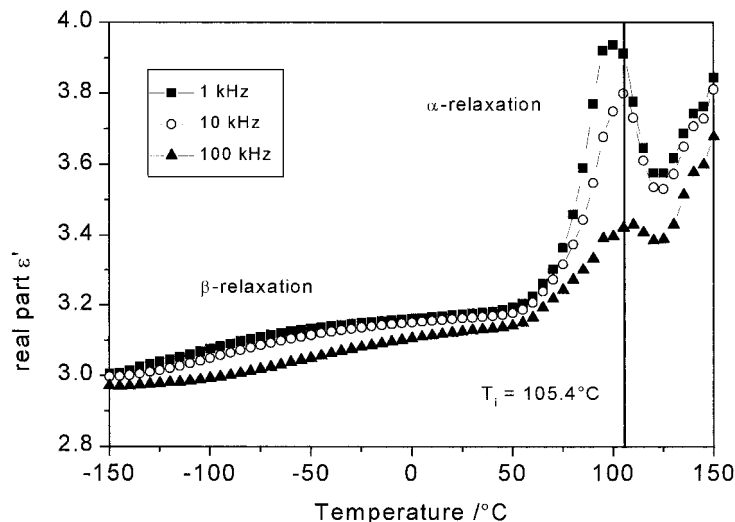


Figure 8. Real part of the dielectric permittivity (ϵ') versus temperature for the β - and α -processes of compound **4a** at different frequencies.

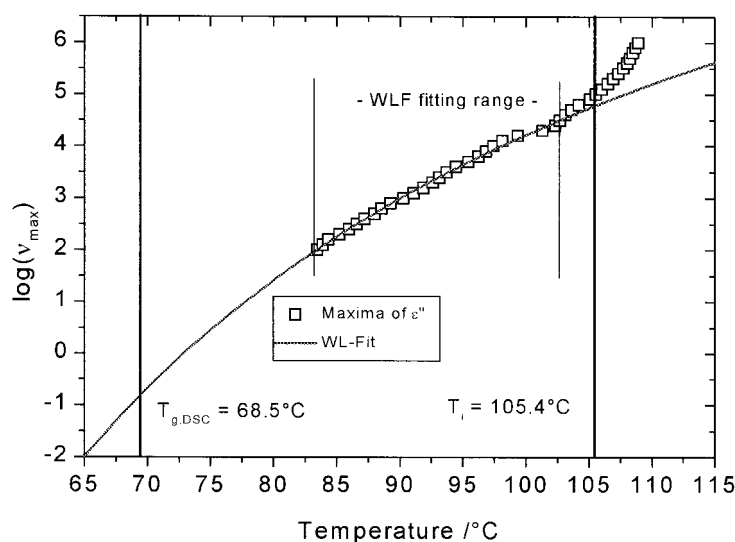


Figure 9. WLF diagram for the α -relaxation of the CT-trimer **4a**.

Table 4. WLF parameters and glass transition temperatures (dielectric spectroscopy (DK) and DSC) for the CT-trimers.

Compound	C_1	$C_2/^\circ\text{C}$	$T_{g,DK}/^\circ\text{C}$	$T_{g,DSC}/^\circ\text{C}$
4a	16.2	56.2	64.9	68.5
4b	10.9	19.1	79.0	79.5
4c	13.7	44.4	-33.2	-26.7

transition from the ordered mesophase to the isotropic melt takes place.

3. Conclusions

We have synthesized the first members of a novel family of donor-acceptor triple compounds based on flat electron-rich penta-alkyne and nitrofluorenone subunits linked chemically via a rod-like azobenzene moiety. The mesophases formed by the CT-trimers **4a,b** correspond to a nematic columnar (N_{CoI}) arrangement. The

individual columns are formed through an intercalated stacking of the flat donor and acceptor units of different molecules. The rod-like groups are oriented more or less perpendicular to the column axis. However, the formation of mixed donor-acceptor stacks due to intermolecular CT-interactions may occur without significant steric hindrance only in the case that the length of the spacer between the acceptor and the calamitic groups exceeds the length of the alkyl substituent attached peripherally to the penta-alkyne donor molecular part. This subtle balance between steric effects and intermolecular charge-transfer interactions leads to the disappearance of mesomorphic properties in the case of the five-fold pentyl substituted triple compound **4c**. Nevertheless, it seems obvious that the concept of linking chemically three structural elements differing in shape and functionality offers a powerful means of obtaining novel thermotropic mesophases combining features of calamitic phases with those of columnar liquid crystalline structures.

4. Experimental

4.1. Materials

4.1.1. Sulphonated pentakis(phenylethynyl)benzene derivatives **2**

A mixture consisting of 1.0 mmol of the appropriate hydroxyundecyl pentakis(phenylethynyl)phenyl ether **1** [11], 0.3 g (1.71 mmol) of benzenesulphonyl chloride, 0.2 g (2.53 mmol) of pyridine and 8 ml of dichloromethane was stirred under a nitrogen atmosphere at 0°C for 30 min followed by stirring at room temperature for 24 h. Afterwards the reaction mixture was washed with 2M hydrochloric acid. The organic solution was dried with sodium sulphate and the solvent was removed under reduced pressure. The residual crude products **2** were purified by flash chromatography using Kieselgel 60, 230–400 mesh (E. Merck, Darmstadt) using light petroleum/ethyl acetate (10:3) as eluent.

4.1.1.1. 11-[Pentakis(phenylethynyl)phenoxy]undecyl benzenesulphonate **2a**

Yield 95.0%, C₆₃H₅₂O₄S (*M_w* 905.2), m.p. 102.5°C. IR (KBr): $\nu = 2210$ (C≡C), 1360 (SO₂), 1170 (SO₂) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 1.17–1.35 (m, 12H, CH₂), 1.62 (m, 4H, CH₂), 1.93 (m, 2H, CH₂), 4.03 (t, 2H, CH₂–O–SO₂, *J* = 6.5 Hz), 4.39 (t, 2H, CH₂–O–phenyl, *J* = 6.3 Hz), 7.38 (m, 15H, phenyl), 7.54–7.64 (m, 10H, phenyl and 3H, phenyl–SO₂), 7.90 (d, 2H, phenyl–SO₂, *J* = 8.1 Hz).

4.1.1.2. 11-[Pentakis(4-methylphenylethynyl)phenoxy]-undecyl benzenesulphonate **2b**

Yield 84.0%, C₆₈H₆₂O₄S (*M_w* 975.3), m.p. 139.0°C. IR (KBr): $\nu = 2210$ (C≡C), 1360 (SO₂), 1170 (SO₂) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 1.17–1.34 (m, 12H, CH₂), 1.61 (m, 4H, CH₂), 1.91 (m, 2H, CH₂), 2.39 (s, 15H, CH₃), 4.03 (t, 2H, CH₂–O–SO₂, *J* = 6.5 Hz), 4.36 (t, 2H, CH₂–O–phenyl, *J* = 6.3 Hz), 7.17 (m, 10H, phenyl), 7.48–7.63 (m, 10H, phenyl and 2H, phenyl–SO₂), 7.90 (d, 2H, phenyl–SO₂, *J* = 7.3 Hz), 8.04 (d, 1H, phenyl–SO₂, *J* = 7.5 Hz).

4.1.1.3. 11-[Pentakis(4-pentylphenylethynyl)phenoxy]-undecyl benzenesulphonate **2c**

Yield 76.4%, C₈₈H₁₀₂O₄S (*M_w* 1255.8), m.p. 56.0°C. IR (KBr): $\nu = 2210$ (C≡C), 1360 (SO₂), 1170 (SO₂) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 0.91 (t, 15H, CH₃, *J* = 6.7 Hz), 1.25–1.69 (m, 30H, CH₂, pentyl chains and 16H, CH₂, undecyl chain), 1.92 (m, 2H, CH₂, undecyl chain), 2.63 (t, 10H, CH₂, pentyl chains, *J* = 7.6 Hz), 4.03 (t, 2H, CH₂–O–SO₂, *J* = 6.5 Hz), 4.36 (t, 2H, CH₂–O–phenyl, *J* = 6.3 Hz), 7.17 (m, 10H, phenyl), 7.53 (m, 10H, phenyl), 7.63 (m, 2H, phenyl–SO₂), 7.76 (m, 1H, phenyl–SO₂), 8.05 (d, 2H, phenyl–SO₂, *J* = 7.5 Hz).

4.1.2. Non-symmetric dimers **3** incorporating a flat penta-alkyne and a rod-shaped azobenzene moiety

Under a nitrogen atmosphere a mixture containing 0.21 g (0.87 mmol) of 4-(4-hydroxyphenylazo)benzoic acid [24], 0.22 g (0.94 mmol) of potassium carbonate and 4 ml of dry dimethylformamide was heated with stirring at 100°C for 1 h. Then 0.87 mmol of the appropriate sulphonated penta-alkyne derivative **2**, dissolved in 2 ml of dimethylformamide, was added and the mixture was stirred and heated at 100°C for an additional 4 h. After cooling to room temperature, the reaction mixture was poured into ice/water; the precipitate was collected by filtration, washed with water and dried in vacuum. Purification of the products **3** was performed by flash chromatography; details are given below.

4.1.2.1. 11-[Pentakis(phenylethynyl)phenoxy]undecyl 4-(4-hydroxyphenylazo)benzoate **3a**

One flash chromatogram with light petroleum/ethyl acetate (10:3.5) as eluent; one flash chromatogram with light petroleum/dichloromethane (7:10) as eluent. Yield 31.0%, C₇₀H₅₆N₂O₄ (*M_w* 989.2), m.p. 62.5°C. IR (KBr): $\nu = 2210$ (C≡C), 1715 (COO) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 1.17–1.40 (m, 12H, CH₂), 1.63 (m, 2H, CH₂), 1.78 (m, 2H, CH₂), 1.94 (m, 2H, CH₂), 4.34 (t, 2H, CH₂–O–CO, *J* = 6.6 Hz), 4.39 (t, 2H, CH₂–O–phenyl, *J* = 6.3 Hz), 6.96 (d, 2H, azobenzene, *J* = 8.7 Hz), 7.37 (m, 15H, phenyl), 7.62 (m, 10H, phenyl), 7.90 (d, 4H, azobenzene, *J* = 8.4 Hz), 8.17 (d, 2H, azobenzene, *J* = 8.4 Hz).

4.1.2.2. 11-[Pentakis(4-methylphenylethynyl)phenoxy]-undecyl 4-(4-hydroxyphenylazo)benzoate **3b**

One flash chromatogram with light petroleum/ethyl acetate (10:2.5) as eluent; one flash chromatogram with light petroleum/dichloromethane (1:1) as eluent. Yield 50.0%, C₇₅H₆₆N₂O₄ (*M_w* 1059.4), m.p. 144.5°C. IR (KBr): $\nu = 2210$ (C≡C), 1715 (COO) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 1.26–1.96 (m, 18H, CH₂), 2.39 (s, 15H, CH₃), 4.33 (t, 2H, CH₂–O–CO, *J* = 6.7 Hz), 4.36 (t, 2H, CH₂–O–phenyl, *J* = 6.7 Hz), 6.95 (d, 2H, azobenzene, *J* = 8.8 Hz), 7.16 (m, 10H, phenyl), 7.50 (m, 10H, phenyl), 7.89 (d, 4H, azobenzene, *J* = 8.8 Hz), 8.16 (d, 2H, azobenzene, *J* = 8.5 Hz).

4.1.2.3. 11-[Pentakis(4-pentylphenylethynyl)phenoxy]-undecyl 4-(4-hydroxyphenylazo)benzoate **3c**

One flash chromatogram with light petroleum/ethyl acetate (10:2.5) as eluent; one flash chromatogram with light petroleum/dichloromethane (1:1) as eluent. Yield 63.3%, C₉₅H₁₀₆N₂O₄ (*M_w* 1339.9), m.p. 85.0°C. IR (KBr): $\nu = 2210$ (C≡C), 1715 (COO) cm⁻¹. ¹H NMR (CDCl₃): δ (ppm) = 0.86 (t, 15H, CH₃, *J* = 6.6 Hz),

1.18–1.64 (m, 30H, CH₂, pentyl chains and 16H, CH₂, undecyl chain), 1.82 (m, 2H, CH₂, undecyl chain), 2.60 (t, 10H, CH₂, pentyl chains, *J* = 7.5 Hz), 4.17 (t, 2H, CH₂–O–CO, *J* = 5.0 Hz), 4.31 (t, 2H, CH₂–O–phenyl, *J* = 6.0 Hz), 6.90 (d, 2H, azobenzene, *J* = 8.8 Hz), 7.18 (m, 10H, phenyl), 7.43 (m, 10H, phenyl), 7.80 (m, 4H, azobenzene), 8.05 (d, 2H, azobenzene, *J* = 9.1 Hz).

4.1.3. *Pentayne based donor–acceptor triple compounds 4*

To prepare the non-symmetric trimers **4**, 0.424 mmol of the appropriate compound **3** and 0.12 g (1.27 mmol) of 3-(2,4,7-trinitro-9-fluorenylideneaminoxy)propionic acid [5] were dissolved in 4 ml of dry dioxan. After the addition of 3 ml of dry dichloromethane, the mixture was cooled to 0°C. While stirring the mixture under a nitrogen atmosphere, 5 mg of 4-dimethylaminopyridine in 0.5 ml of CH₂Cl₂ were added followed by the dropwise addition of 0.27 g (1.27 mmol) of *N,N'*-dicyclohexylcarbodiimide dissolved in 1 ml of CH₂Cl₂. Stirring was continued at ambient temperature for 70 h. The resulting precipitate was removed by filtration and washed with CH₂Cl₂. The combined solutions were evaporated in vacuum. The products were purified by flash chromatography using light petroleum/ethyl acetate (10:3), ethanol and dichloromethane successively as eluents. The phase transition temperatures of the compounds **4** are collected in table 1.

4.1.3.1. *11-[Pentakis(phenylethynyl)phenoxy]undecyl 4-{4-[3-(2,4,7-trinitro-9-fluorenylideneaminoxy)propanoyloxy]phenylazo}benzoate 4a*

Yield 72.0%, C₈₆H₆₄N₆O₁₂ (*M_w* 1373.5). IR (KBr): $\nu = 2210$ (C≡C), 1760 (COO), 1720 (COO), 1530 (NO₂), 1350 (NO₂) cm⁻¹. ¹H NMR (CDCl₃) δ (ppm) = 1.26–1.45 (m, 12H, CH₂), 1.60 (m, 2H, CH₂), 1.78 (m, 2H, CH₂), 1.90 (m, 2H, CH₂), 3.15 (t, 2H, CH₂–CO–O, *J* = 6.2 Hz), 4.31 (t, 2H, CH₂–O–CO, *J* = 6.5 Hz), 4.34 (t, 2H, CH₂–O–phenyl, *J* = 6.8 Hz), 4.90 (t, 2H, CH₂–O–N, *J* = 6.2 Hz), 7.26 (m, 2H, azobenzene), 7.38 (m, 15H, phenyl), 7.59 (m, 10H, phenyl), 7.93 (m, 4H, azobenzene), 8.17 (d, 2H, azobenzene, *J* = 8.5 Hz), 8.25–9.13 (m, 5H, TNF).

4.1.3.2. *11-[Pentakis(4-methylphenylethynyl)phenoxy]undecyl 4-{4-[3-(2,4,7-trinitro-9-fluorenylideneaminoxy)propanoyloxy]phenylazo}benzoate 4b*

Yield 11.0%, C₉₁H₇₄N₆O₁₂ (*M_w* 1443.5). IR (KBr): $\nu = 2210$ (C≡C), 1760 (COO), 1720 (COO), 1530 (NO₂), 1340 (NO₂) cm⁻¹. ¹H NMR (CDCl₃) δ (ppm) = 1.27–1.60 (m, 14H, CH₂), 1.78 (m, 2H, CH₂), 1.90 (m, 2H, CH₂), 2.39 (s, 15H, CH₃), 3.21 (t, 2H, CH₂–CO–O, *J* = 6.0 Hz), 4.30 (t, 2H, CH₂–O–CO, *J* = 6.3 Hz), 4.35 (t, 2H, CH₂–O–phenyl, *J* = 6.6 Hz), 4.97 (t, 2H, CH₂–O–N,

7.15–7.31 (m, 2H, azobenzene and 10H, phenyl), 7.48 (m, 10H, phenyl), 7.92 (d, 2H, azobenzene, *J* = 8.5 Hz), 7.97 (d, 2H, azobenzene, *J* = 8.7 Hz), 8.18 (d, 2H, azobenzene, *J* = 8.5 Hz), 8.30–9.18 (m, 5H, TNF).

4.1.3.3. *11-[Pentakis(4-pentylphenylethynyl)phenoxy]undecyl 4-{4-[3-(2,4,7-trinitro-9-fluorenylideneaminoxy)propanoyloxy]phenylazo}benzoate 4c*

Yield 9.8%, C₁₁₁H₁₁₄N₆O₁₂ (*M_w* 1724.2). IR (KBr): $\nu = 2210$ (C≡C), 1760 (COO), 1720 (COO), 1530 (NO₂), 1340 (NO₂) cm⁻¹. ¹H NMR (CDCl₃) δ (ppm) = 0.87 (t, 15H, CH₃, *J* = 6.5 Hz), 1.14–1.64 (m, 30H, CH₂, pentyl chains and 16H, CH₂, undecyl chain), 1.81 (m, 2H, CH₂, undecyl chain), 2.60 (t, 10H, CH₂, pentyl chains, *J* = 7.3 Hz), 2.86 (t, 2H, CH₂–CO–O, *J* = 6.0 Hz), 4.27 (m, 2H, CH₂–O–CO and 2H, CH₂–O–phenyl), 4.79 (t, 2H, CH₂–O–N, *J* = 6.0 Hz), 6.93 (d, 2H, azobenzene, *J* = 8.8 Hz), 7.19 (m, 10H, phenyl), 7.41 (m, 10H, phenyl), 7.81 (d, 2H, azobenzene, *J* = 8.9 Hz), 7.84 (d, 2H, azobenzene, *J* = 8.6 Hz), 8.08 (d, 2H, azobenzene, *J* = 8.5 Hz), 8.21–9.04 (m, 5H, TNF).

4.2. Methods for characterization

The purity of compounds **2–4** was checked by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC). HPLC analyses were performed on RP 18 columns (Bischof, Nucleosil 100) using HPLC equipment (Bischof) fitted with an UV-detector, Lambda 100 ($\lambda = 254$ nm). IR spectra were obtained with an M 80 spectrometer (Carl Zeiss Jena). ¹H NMR spectra were recorded using a Bruker AMX 300 spectrometer. Optical texture observations were made with an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage fitted with a Linkam TP 92 control unit and a Linkam LNP 1 liquid nitrogen cooling system. Photomicrographs were obtained using an Olympus OM-4 Ti system camera. Differential scanning calorimetry was carried out with a Netzsch DSC 200. Wide angle scattering analysis was performed employing a goniometer from Siemens (D 5000). Dielectric measurements were made using a Hewlett-Packard Impedance Analyzer HP 4284 A and covering a frequency range from 100 Hz to 1 MHz. The experimental set-up is described in detail elsewhere [25].

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